A Preliminary Assessment of Sources of Nitrate in Springwaters, Suwannee River Basin, Florida

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Prepared in cooperation with the

Suwannee River Water Management District

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By Brian G. Katz and H. David Hornsby

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Tallahassee, Florida
1998

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
Mass		
pound avoirdupois (lb avdp)	0.4536	kilogram (kg)
Specific capacity		
gallon per minute per foot [(gal/min)/ft)]	0.207	liter per second per meter [(L/s)/m]
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)
Hydraulic gradient		
foot per mile (ft/mi)	0.1786	meter per kilometer (m/km)
Flow		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=1.8\ °C+32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Altitude, as used in this report, refers to distance above or below sea level.

Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [$(ft^3d)/ft^2$]ft. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

ADDITIONAL ABBREVIATIONS

L	liter
µm	micrometer
mg/L	milligrams per liter
bls	below land surface
DOC	dissolved organic carbon
IAEA	International Atomic Energy Agency
pg/kg	picograms per kilogram
pptv	parts per trillion by volume
TU	tritium units
SRWMD	Suwannee River Water Management District
USGS	U.S. Geological Survey

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Abstract

A cooperative study between the Suwannee River Water Management District (SRWMD) and the U.S. Geological Survey (USGS) is evaluating sources of nitrate in water from selected springs and zones in the Upper Floridan aquifer in the Suwannee River Basin. A multi-tracer approach, which consists of the analysis of water samples for naturally occuring chemical and isotopic indicators, is being used to better understand sources and chronology of nitrate contamination in the middle Suwannee River region. In July and August 1997, water samples were collected and analyzed from six springs and two wells for major ions, nutrients, and dissolved organic carbon. These water samples also were analyzed for environmental isotopes [$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$] to determine sources of water and nitrate. Chlorofluorocarbons (CFCs; CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) and tritium (^3H) were analyzed to assess the apparent ages (residence time) of springwaters and water from the Upper Floridan aquifer.

Delta ^{15}N-NO_3 values in water from the six springs range from 3.94 per mil (Little River Springs) to 8.39 per mil (Lafayette Blue Spring). The range of values indicates that nitrate in the sampled springwaters most likely originates from a mixture of inorganic (fertilizers) and organic (animal wastes) sources, although the higher delta ^{15}N-NO_3 value for Lafayette Blue Spring indicates that an organic source of nitrogen is likely at this site. Water samples from the two wells sampled in Lafayette County have high delta ^{15}N-NO_3 values of 10.98 and 12.1 per mil, indicating the likelihood of an organic source of nitrate. These two wells are located near dairy and poultry farms, where leachate from animal wastes may contribute nitrate to ground water. Based on analysis of CFCs in ground water, the mean residence time of water in springs ranges from about 12 to 25 years. CFC-modeled recharge dates for water samples from the two shallow zones in the Upper Floridan aquifer range from 1985 to 1989.

INTRODUCTION

In the middle Suwannee River region in northern Florida, elevated concentrations of nitrate have been measured in well water from the Upper Floridan aquifer and springwaters discharging into the Suwannee River from Dowling Park, Fla., to Branford, Fla., (fig. 1). Mean nitrate-N concentrations increase nearly four-fold from 0.15 mg/L at Suwannee Springs, Fla., (150 mi from mouth of river) to 0.57 mg/L at Branford (76 mi from river mouth) (Katz and others, 1997). The increase in nitrate in river water at Branford is attributed to ground-water discharge because there are no major stream inputs to the middle Suwannee River in this region. Also, the concentration of nitrate in river water is inversely related to discharge; that is, concentrations are higher during base flow conditions when the contribution from ground water is greatest (Hornsby and Mattson, 1996). A recently completed study of the contribution of springs to nitrate loads and water quantity along a 33-mi reach of the Suwannee River during base flow conditions found that river nitrate-N loads increased downstream from 2,300 kg/d just downstream

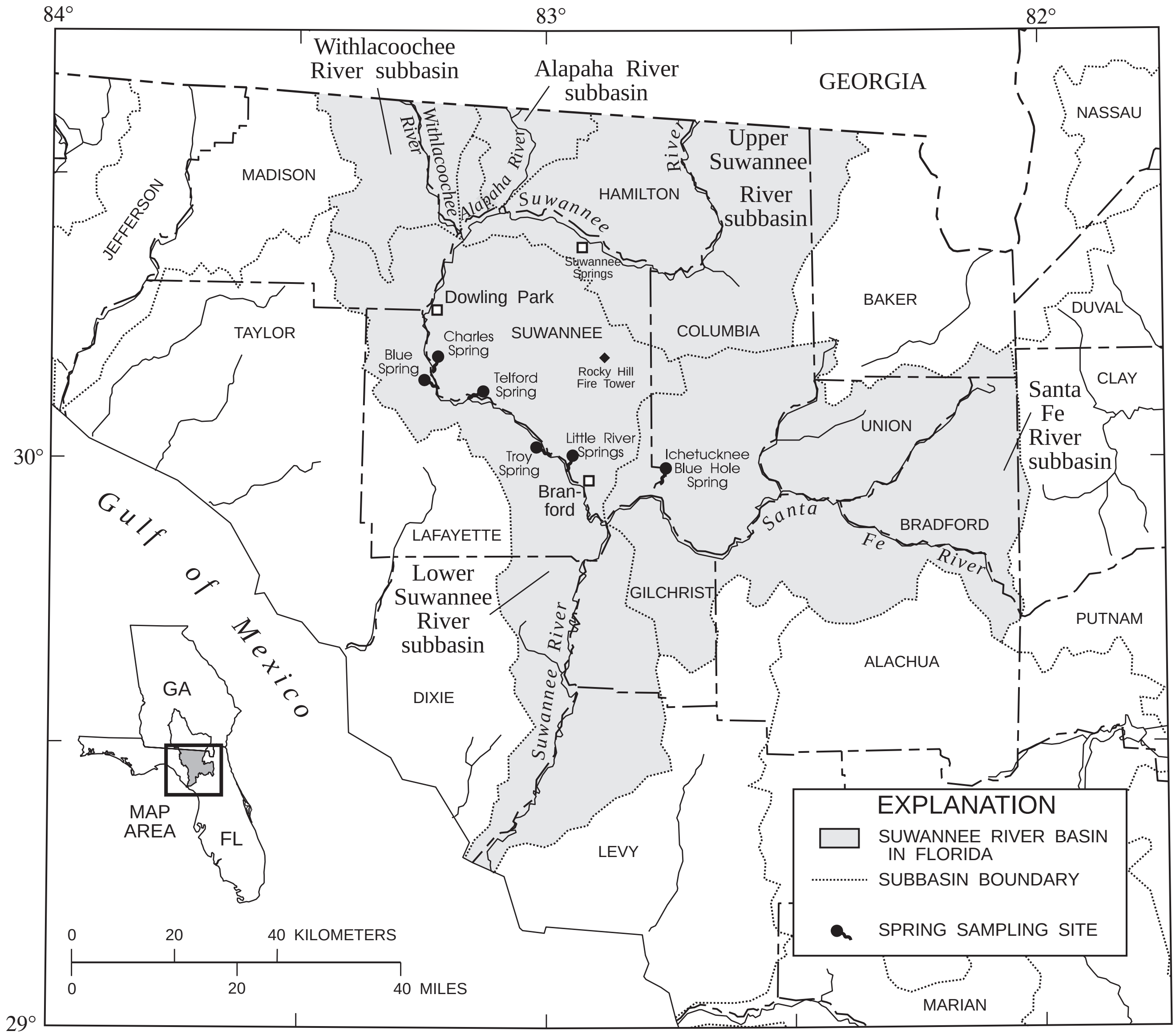

Figure 1. Study area showing location of sampled springs.

of Dowling Park to 6,000 kg/d at Branford (Pittman and others, 1997). Nearly 90 percent of the increase in nitrate load occurred in the lower two-thirds of the reach and was attributed mainly to upward diffuse leakage of ground water through the riverbed (Pittman and others, 1997). Nitrate-N concentrations in several springs that discharge into the Suwannee River along this middle reach of the Suwannee River typically range from about 2 to 19 mg/L (Hornsby and Mattson, 1998). Nitrate-N concentrations in water from the Upper Floridan aquifer (less than 120 ft below land surface) in parts of Suwannee and Lafayette Counties exceed the maximum contaminant level of 10 mg/L for drinking water (U.S. Environmental Protection Agency, 1990). These elevated nitrate concentrations in ground water and springwater greatly exceed natural background levels of nitrate-N in the Upper Floridan aquifer in the Suwannee River Basin area that are 0.05 mg/L or less (Katz, 1992; Maddox and others, 1992).

At present, little information exists to determine the source(s) and fate of nitrate in the Upper Floridan aquifer along the middle reach of the Suwannee River. The Suwannee River has been designated an outstanding Florida waterbody. However, increases in nitrate concentrations from human activities may be causing adverse ecological effects, which are indicated by an increase in periphyton biomass along this reach (Hornsby and Mattson, 1996). Also of concern are the effects of high nitrate concentrations in the Suwannee River on the estuary of the river system, which is also designated an outstanding Florida waterbody and is a State Aquatic Preserve and a National Wildlife Refuge.

Purpose and Scope

This report presents the results of a cooperative effort between the Suwannee River Water Management District (SRWMD) and the U.S. Geological Survey (USGS), to evaluate sources of nitrate in water from selected springs and zones within the Upper Floridan aquifer in the Suwannee River Basin. A multi-tracer approach, which consists of the analysis of water samples for naturally-occurring chemical and isotopic indicators, is used in this study to better understand the sources and chronology of nitrate contamination in the middle Suwannee River region. This report presents the results of the first phase of the study, in which water samples were collected in July and August 1997 from six springs and two wells. These samples were analyzed for major ions, nutrients, and dissolved organic carbon (DOC). Water samples also were analyzed for selected environmental isotopes [$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$] to determine sources of water and nitrate. To better understand when nitrate entered the ground-water system, water samples are analyzed for chlorofluorocarbons (CFCs; CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) and tritium (^3H) to assess the apparent ages (residence time) of springwaters and water from the Upper Floridan aquifer.

Acknowledgments

This study was funded jointly by the U.S. Geological Survey and the Suwannee River Water Management District. The authors thank Johnkarl Bohlke, USGS, for nitrogen isotope analyses; Robert L. Michel, USGS, for tritium analyses; Julian Wayland, USGS, for help with water sampling; and Marian P. Berndt, USGS, Gregg W. Jones, SWFWMD, and Edward.T. Oaksford, USGS, for their review comments that were helpful in revising this report.

METHODS

Samples of water from five springs along the Suwannee River and two wells in the study area were collected during low-flow conditions on July 15-16, 1997. Springs that were sampled included Telford Spring, Blue Spring (Lafayette County), Charles Spring, Troy Spring, and Little River Springs (fig. 1). These springs were selected for sampling because previous data indicated that high loads of nitrate were being discharged to the Suwannee River in this area (Hornsby and Mattson, 1996). Water samples also were collected from Blue Hole Spring (fig. 1) in the Ichnetucknee Springs State Park on August 14, 1997, as part of a study to determine the rate of ground-water flow in

the Ichetucknee River Basin. Water samples were collected from relatively shallow zones in the Upper Floridan aquifer from two wells near the Suwannee River in Lafayette County (fig. 2) located in an area of agricultural land-use. Well -051209001 is screened from 24 to 44 ft below land surface (bls) and well -051216011 is screened from 84 to 105 ft bls. These two wells are part of a statewide network designed to study the effects of different land uses on ground-water quality. These two wells were chosen because of differences in depth and previous high nitrate concentrations (10 to 20 mg/L as N in water samples collected in 1994 and 1996).

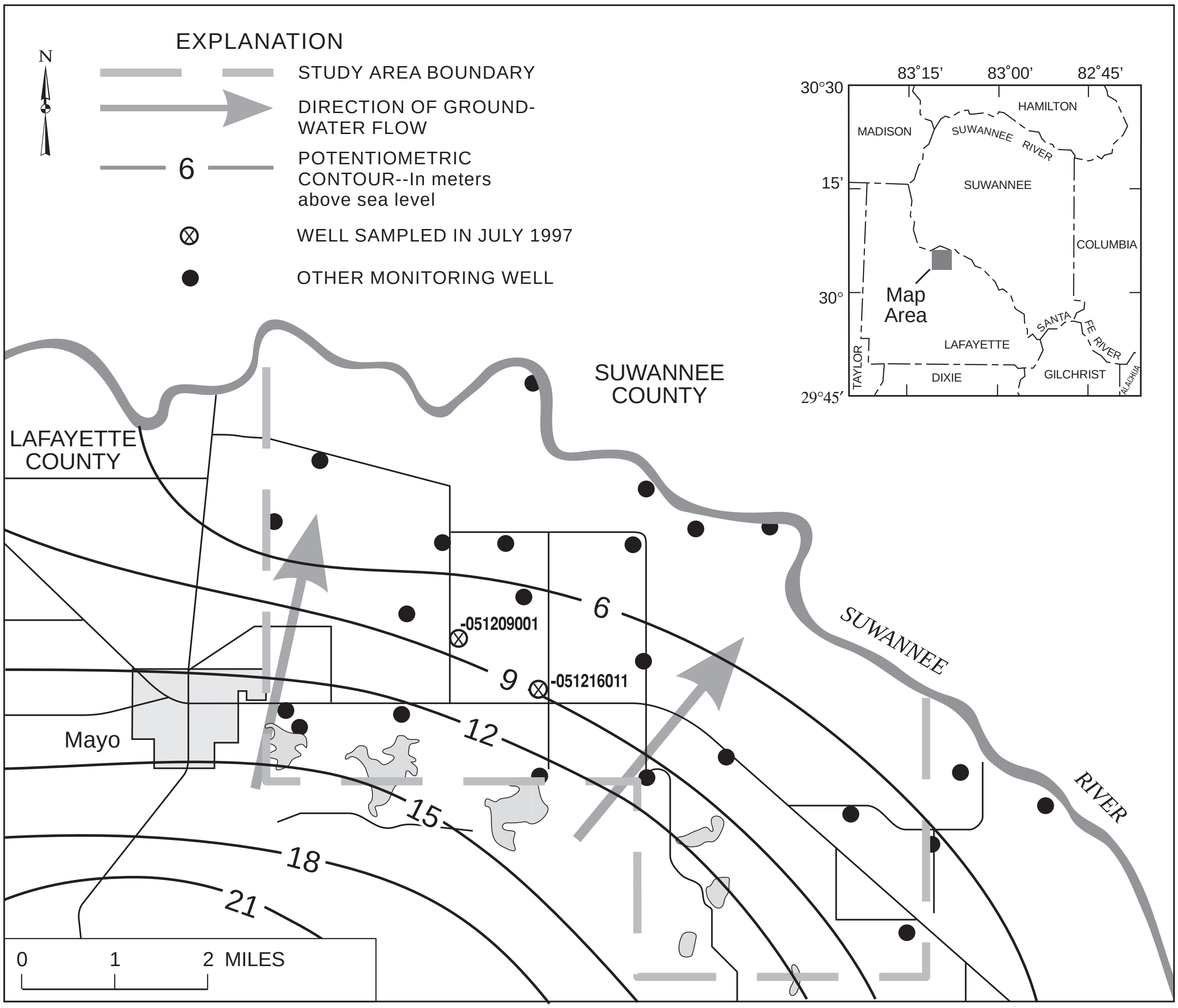

Figure 2. Agricultural study area in Lafayette County showing location of wells sampled.

Sample Collection

Spring-water samples were collected using a positive displacement dual piston (Bennett) pump with a 0.95-cm Teflon discharge line at pumping rates of approximately 0.06 L/s. Sampling methodology varied somewhat depending on accessibility to the spring and site characteristics. Water samples were collected from Troy Spring and Little River Springs from a boat, whereas samples from the other four springs were collected from the adjacent shoreline. At the spring sites, the pump head was lowered between 5 and 17 m beneath the water surface into the spring vent. At well site -051209001, the Bennett pump intake was positioned approximately 1 to 2 m above the open interval in the well after three casing volumes were purged using a submersible pump. An in-line submersible pump was used to collect water samples at well -051216011. At all sites, specific conductance, pH, dissolved oxygen, and temperature were measured using a closed flow-through chamber to prevent contact of the ground water with the atmosphere. After field readings of these properties had stabilized, samples of springwater and water from wells were collected for major dissolved species and trace elements using standard techniques (Brown and others, 1970; Wood, 1976; Koterba and others, 1995) that included field filtration using a 0.45-μm membrane filter for major ions, nutrients, silica, and a 0.45-μm silver filter for dissolved organic carbon.

Chemical and Isotopic Tracers

A multi-tracer approach was used in this study to gain a better understanding of the geochemical and hydrologic factors affecting the concentration of nitrate in springs and zones in the Upper Floridan aquifer. Each of the naturally-occurring chemical and isotopic tracers that are being analyzed provides a distinct piece of information about the system (Katz and others, 1995b). The integration of these distinct pieces of information will contribute to an increased understanding of the sources of nitrate and the processes that control its fate in this complex karst system.

Naturally occurring tracers provide information on chemical and hydrologic processes (table 1). For example, the concentrations of major ions, nutrients, and dissolved organic carbon give information on sources and processes that affect the concentration of solutes in water from the Upper Floridan aquifer. The stable isotopes of water, oxygen ($^{18}O/^{16}O$) and hydrogen (D/H), provide information on the origin of the water and mixing of different sources of water. Measurements of carbon isotopes ($^{13}C/^{12}C$) provide information to assess rock-water interaction, mixing of water from different sources, and quantify mass tranfer associated with microbially mediated processes (for example, degradation of organic matter with associated terminal electron accepting processes such as ferric iron reduction, sulfate reduction, and methanogenesis). Nitrogen isotopes ($^{15}N/^{14}N$) were used to evaluate sources of nitrate in ground water. Isotopic values were reported using standard δ (delta) notation (Gonfiantini, 1981), as defined by the following expression:

$$\delta \text{ (per mil, ‰)} = [(R_{sample}/R_{standard}) - 1] \times 1{,}000$$

For $\delta^{18}O$, $R = {}^{18}O/{}^{16}O$; for δD, R = D/H; for $\delta^{13}C$, $R = {}^{13}C/{}^{12}C$, and for $\delta^{15}N$, $R = {}^{15}N/{}^{14}N$.

Age Dating of Waters

The transient tracers, tritium and chlorofluorocarbons (CFCs), were used to estimate the age of ground water. Tritium (^{3}H) analyses provide estimates on the time of ground-water recharge, by comparing measured ^{3}H concentrations in ground water with the long-term ^{3}H input function of rainfall measured at the International Atomic Energy Agency (IAEA) precipitation monitoring station in Ocala, Florida (Michel, 1989) (fig. 3). ^{3}H activity is reported in tritium units (TU), with 1 TU equal to 1 ^{3}H atom in 10^{18} hydrogen atoms and 7.1 disintegrations per minute per gram of water.

Table 1. Principal uses for naturally occurring isotopic and chemical tracers in this study and references for sample collection and analysis

Isotopic or chemical tracer	Principal use in study	References for sample collection and analysis
$^{15}N/^{14}N$	Identify source(s) of nitrate.	Bohlke and Denver (1995)
$^{18}O/^{16}O$; D/H	Identify source(s) of springwater and water from zones in Upper Floridan aquifer; delineate flow patterns.	Coplen (1994); Gonfiantini (1981)
Chlorofluorocarbons CCl_3F (CFC-11) CCl_2F_2 (CFC-12) $C_2Cl_3F_3$ (CFC-113)	Determine age (mean residence time) of springwater and recharge age of water from zones in aquifer.	Busenberg and Plummer (1992)
Tritium (^3H)		Michel (1989)
Dissolved gases (N_2, Ar)	Determine recharge temperature to estimate age of springwaters and water from zones in aquifer.	Busenberg and Plummer (1992)
Major ions, nutrients, dissolved organic carbon; dissolved gases, (CO_2, O_2, H_2S, CH_4)	Identify sources of solutes in spring water and water from aquifer; quantify biogeochemical processes that control the composition of spring-waters and water from zones in the aquifer.	Brown and others (1970); Wood (1976); Koterba and others (1995)
$^{13}C/^{12}C$		Gleason and others (1969); Coplen (1994)

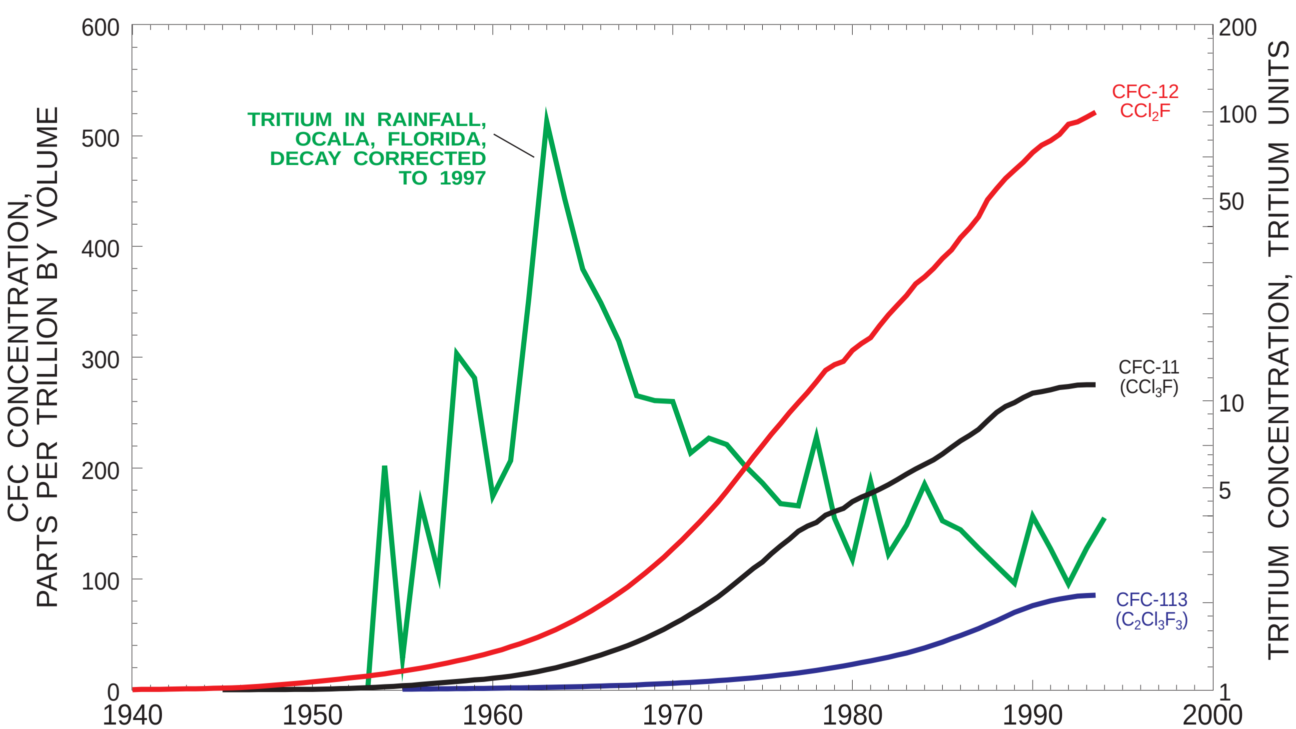

Figure 3. Concentrations of CFC-11, CFC-12, and CFC-113 in the atmosphere, 1940-94 and tritium concentrations in rainfall collected at Ocala, Florida, decay corrected to 1997.

The CFC age-dating technique was used in this study for assessing the apparent age of springwaters and water from zones in the Upper Floridan aquifer. This technique, which has been used to date ground water in northern Florida (Katz and others, 1995a), is based on four main assumptions: (1) the partial pressures of CFCs are the same in both the soil (unsaturated zone) and the tropospheric atmospheres, which is valid for unsaturated zones less than 10 m in thickness (Busenberg and Plummer, 1992), (2) the aquifer has not been contaminated by local, near-surface sources of CFCs commonly found near or in urban areas, (3) the CFC concentration in recharge water is in equilibrium with the CFC partial pressure in the soil atmosphere, and (4) the CFC concentrations in the aquifer have not been altered by biological, geochemical, or hydrologic processes. The stability of CFC compounds in the hydrosphere has led to their effective use as tracers to age date ground water that has been recharged during the past 50 years (Plummer and others, 1993).

The apparent age of springwaters and water from zones in the aquifer is determined from a CFC-modeled recharge date (as defined by Busenberg and Plummer, 1992). A CFC-modeled recharge date is determined on the basis of the equilibrium partitioning between rainwater and the partial pressures of trichlorofluoromethane (CCl_3F, CFC-11), dichlorodifluoromethane (CCl_2F_2, CFC-12), and trichlorotrifluoroethane ($C_2Cl_3F_3$, CFC-113) in the troposphere or soil atmosphere. The CFC dating method actually provides three independent ages, which are based on measured concentrations of each of the three CFC compounds. Ideally, three independent dates are derived and can be used as a cross-check on the sampling and analytical methods. An apparent age of the sampled water is modeled based on the comparison of the measured concentration of each CFC compound with calculated equilibrium partial pressures, using solubility data for each compound with their respective atmospheric growth curve (fig. 3). The concentration of CFCs in ground water is a function of the atmospheric partial pressures and the temperature at the base of the unsaturated zone during recharge. Recharge temperatures are calculated from measurements of dissolved nitrogen and argon concentrations in water samples from each spring and well.

MAJOR IONS AND NUTRIENTS

Water from springs and shallow zones of the Upper Floridan aquifer is a Ca-HCO_3 type with low dissolved solids concentrations ranging from 150 to 246 mg/L (table 2). Dissolved organic carbon concentrations in springwater and ground water are low, typically less than or equal to 1 mg/L (analytical method reporting limit of 0.1 mg/L). Saturation indices of these waters with respect to calcite and dolomite are slightly less than 0.0 indicating that the waters are slightly understaturated with these minerals (table 2). The saturation indices (SI, table 2) were calculated using the computer-based thermodynamic model WATEQF (Plummer and others, 1994), which assumes that all dissolved species are at equilibrium with one another. When ground water is undersaturated with respect to particular minerals in the limestone matrix of the Upper Floridan aquifer, there is the potential for continued dissolution of these minerals.

Nitrate-N concentrations in springwaters ranged from 0.72 mg/L (Ichetucknee Blue Hole Spring) to 2.7 mg/L (Troy Spring). Nitrate-N concentrations in water samples from springs collected during this study were slightly higher than nitrate concentrations measured in water samples from these springs taken previously (Hornsby and Mattson, 1996). In water from the two wells tapping shallow zones of the Upper Floridan aquifer in Lafayette County, nitrate-N concentrations were 18 and 20 mg/L.

The concentrations of other dissolved species, such as sulfate, potassium, and magnesium, also are higher in springwater and water from the two zones in the Upper Floridan aquifer than background concentrations of these species in the Upper Floridan aquifer in the area (Katz, 1992; Maddox and others, 1992). Sulfate concentrations in springwaters and water from the two zones in the Upper Floridan aquifer are elevated by a factor of 3, with the exception of water from Ichetucknee Blue Hole Spring which has sulfate concentrations below background. Concentrations of potassium are more than an order of magnitude higher in water from the two wells in the agricultural area than background potassium concentrations. Magnesium concentrations are slightly higher in springwaters, but by a

Table 2. Chemical properties, concentrations of major ions and other dissolved species, and calcite saturation index for spring waters and ground water.

[Concentrations of elements and species are in milligrams per liter, unless otherwise noted; Temp denotes temperature in degrees Celsius, SC denotes specific conductance in microsiemens per centimeter, DO denotes dissolved oxygen, Discharge of springflow is in cubic feet per second; NA denotes not applicable; DOC denotes dissolved organic carbon; SiO2 denotes dissolved silica; DS denotes dissolved solids; and SI denotes saturation index]

Site name/ Sampling date	Temp °C	pH	SC	DO	Discharge (ft^3/s)	Ca	Mg	Na	K	Cl	SO_4	HCO_3	NO_3-N	DOC	SiO_2	DS	Calcite SI
Charles Spring1 7-15-97	21.6	7.08	370	1.5	16.4	57	10	2.8	0.54	5.1	17	200	2.2	0.8	6.3	190	-0.347
Charles Spring 2 7-15-97	21.6	7.08	370	1.5	16.4	56	10	2.8	0.54	5.1	17	200	2.3	1.0	6.2	189	-0.347
Lafayette Blue Spring 7-15-97	21.8	7.11	423	0.87	84.6	65	11	5.5	0.70	8.7	11	237	2.0	0.9	5.6	218	-0.193
Little River Springs 7-15-97	21.9	7.27	373	1.95	76.1	62	6.9	2.6	0.63	5.9	18	201	1.5	0.4	6.5	195	-0.116
Telford Spring 7-16-97	21.3	7.22	461	3.38	41.6	64	17	3.1	0.41	5.9	44	226	2.5	0.5	7.0	246	-0.138
Troy Spring 7-15-97	22.4	7.20	362	0.38	138	60	6.5	3.0	0.99	6.1	11	196	2.7	0.7	6.4	184	-0.198
Ichetucknee Blue Hole 8-14-97	21.7	7.39	262	2.42	117	51	4.7	2.8	0.37	4.7	4.3	176	0.72	<0.10	9.3	150	-0.120
Well -051209001 7-16-97	23.2	7.12	570	4.10	NA	58	23	12	6.4	14	16	225	18	0.8	7.4	240	-0.252
Well -051216011 7-16-97	22.6	7.21	560	4.38	NA	71	17	8.3	6.2	15	20	203	20	0.5	6.5	236	-0.132

factor of 3 to 4 higher in the two sampled zones of the Upper Floridan aquifer. The elevated concentrations of sulfate, potassium, and magnesium in springwater and ground water indicates the likely contribution from anthropogenic sources (such as fertilizers, leachate from animal wastes, and septic tanks).

SOURCES OF SPRINGWATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

Values of $\delta^{18}O$ and δD in springwaters plot along the global meteoric water line (fig. 4) indicating that they are little affected by evaporation or mixing with surface waters that would have an enriched isotopic signature due to evaporation. Since springwater is representative of ground water that is integrated both temporally and spatially with rainfall recharging the Upper Floridan aquifer, one would expect its stable isotopic composition to plot along the global meteoric water line. Similar values of $\delta^{18}O$ and δD were observed for monthly-composite samples of rainfall collected from June 1995 through May 1996 at the Rocky Hill Fire Tower (from a wet/dry atmospheric deposition collector). Values of δD and $\delta^{18}O$ are slightly enriched (higher) in water from well -051216011 (table 3), indicating that water recharging the aquifer at this site could have undergone some evaporation or that mixing has occurred with surface water that contains an enriched isotopic signature.

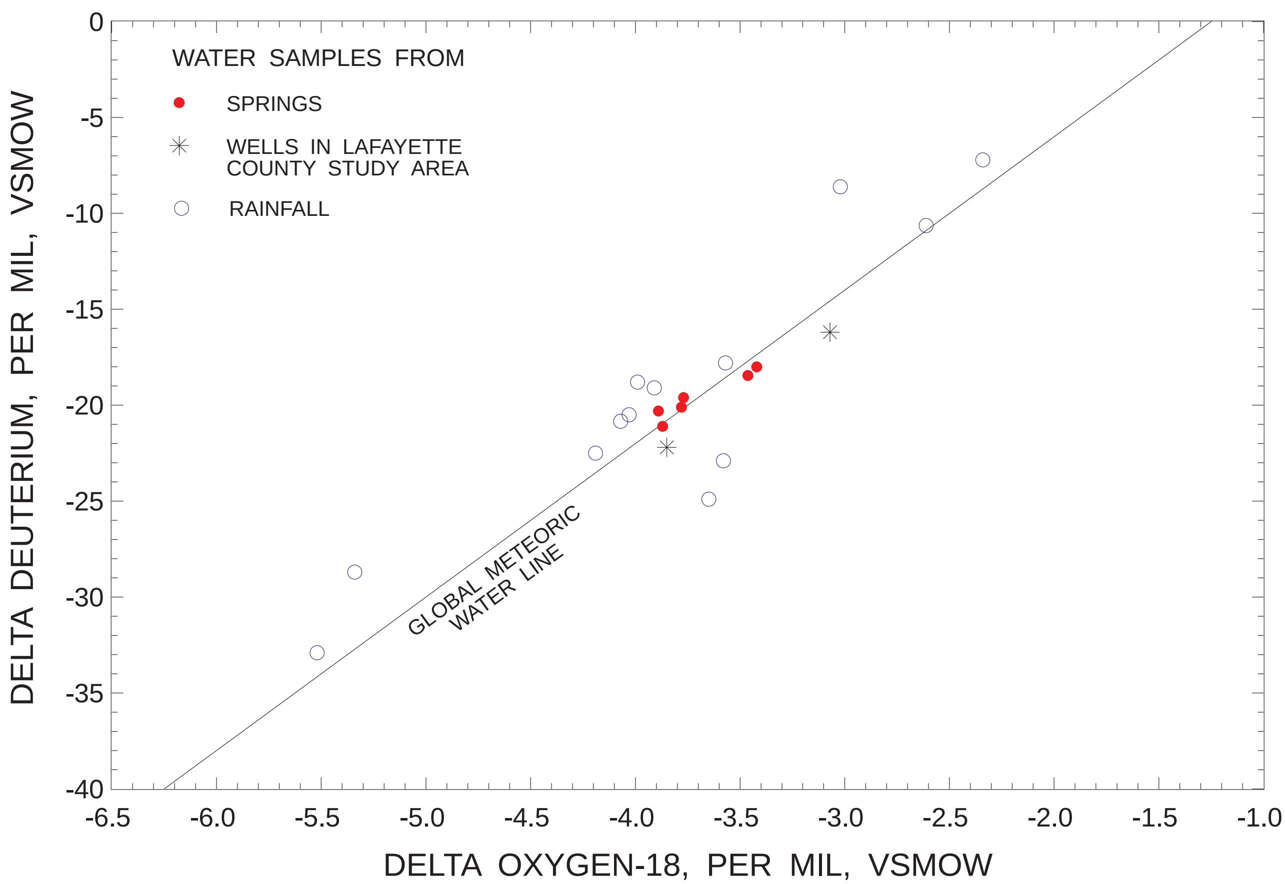

Figure 4. Deuterium and oxygen-18 content of springwater, ground water, and rainfall compared to the global meteoric water line.

Table 3. Isotopic composition of spring waters and ground water
[Delta (d) values are in per mil, Tritium concentrations are in tritium units]

Site name	$\delta^{13}C$	δD	$\delta^{18}O$	$\delta^{15}N$	Tritium
Charles Spring1	-12.88	-19.3	-3.75	4.36	4.4
Charles Spring 2	-13.24	-19.9	-3.80	4.41	4.8
Lafayette Blue Spring	-12.60	-18.0	-3.42	8.39	4.0
Little River Springs	-12.00	-21.1	-3.87	3.94	4.2
Telford Spring	-12.35	-20.3	-3.89	5.81	4.9
Troy Spring	-12.30	-20.1	-3.78	5.40	4.0
Ichetucknee Blue Hole	-12.	-18.6	-3.48	4.36	5.8
Well -051209001	-8.30	-22.2	-3.85	10.98	4.0
Well -051216011	-9.69	-16.2	-3.07	12.12	4.4

SOURCES OF NITRATE IN SPRINGWATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

Values of $\delta^{15}N$ of nitrate have been used to identify sources of nitrate contamination in ground water for more than 20 years (Hornsby, 1986). The method has been used succesfully in areas with thin and permeable unsaturated zones with a shallow water table (Heaton, 1986) and in mantled karst aquifers (Wells and Krothe, 1989; Andrews, 1994; Hornsby, 1994). Delta ^{15}N values for NO_3 in water from the six springs range from 3.94 per mil, Little River Springs, to 8.39 per mil, Lafayette Blue Spring (table 3). The range of values indicates that nitrate in the sampled springwaters most likely originates from a mixture of inorganic (fertilizers) and organic (animal wastes) sources; although the higher $\delta^{15}N$ value for Lafayette Blue Spring indicates the likelihood that nitrate originates from an organic source at this site.

As part of a study of nitrate in ground water near four dairy farms in Lafayette and Suwannee Counties, Andrews (1994) reported the following values of $\delta^{15}N$ of nitrate (per mil) for water samples collected in May 1993 from Lafayette County Blue Spring, 9.65 per mil; Telford, 7.70 per mil; and Convict Springs, 8.90 per mil. Organic sources of nitrogen from leachate of livestock wastes and septic tanks were inferred to be the predominant source of nitrate to springwater (Andrews, 1994). $\delta^{15}N$ values reported by Andrews (1994) are about 1 to 2 per mil higher for Blue and Telford Springs than nitogen isotope data collected during the present study (fig. 5), and can be indicative of the temporal variability in isotopic data. However, the variability in nitrogen isotope values can also reflect the different analytical procedures used by the two laboratories.

Water samples from the two wells sampled in Lafayette County have higher values of delta ^{15}N of NO_3, 10.98 and 12.12 per mil, indicating that an organic source of nitrate is likely. These two wells are located near dairy and poultry farms, where leachate from animal wastes may contribute nitrate to ground water. In shallow ground water, Andrews (1994) found that the source of nitrate tended to be leachate from livestock waste, whereas nitrate in deeper ground water was affected more by leachate from synthetic fertilizers. Based on nitrogen-isotope analyses of water from 66 monitoring and drinking-water wells from the middle Suwannee River basin, Hornsby (1994) found that water from four wells produced delta ^{15}N of NO_3 values that were equal to or

greater than 10 per mil and indicated an organic N source. Hornsby (1994) found that three of the four wells were located downgradient from dairy or poultry operations, indicating the likelihood of localized sources of animal wastes. The majority of wells (44 of 66) yielded water with delta ^{15}N- NO_3 values that were less than or equal to 2 per mil, indicating that inorganic N (synthetic fertilizers) was the dominant source of N in the middle Suwannee River basin. It is important to note that water samples from the 66 wells were withdrawn from zones typically not near the top of the Upper Floridan aquifer and, therefore, may not reflect most recent nitrate contamination (Hornsby, 1994).

The nitrogen-isotope data from the various studies in the middle Suwannee River basin tend to support information on nitrogen inputs to the study area. For 1996-97, Hornsby and Mattson (1998) estimate that 14 and 29 million pounds per year of nitrogen are added to Lafayette and Suwannee Counties, respectively, from various sources (fertilizers, animal wastes, atmospheric deposition). In Lafayette County, animal wastes from farming operations (not corrected for losses such as volatilization and mineralization in the soil) and fertilizers contributed about 53 and 39 percent of the total N input, respectively. In contrast, fertilizers and animal wastes from farming operations in Suwannee County contributed about 49 and 45 percent of the total N input, respectively (Hornsby and Mattson, 1998).

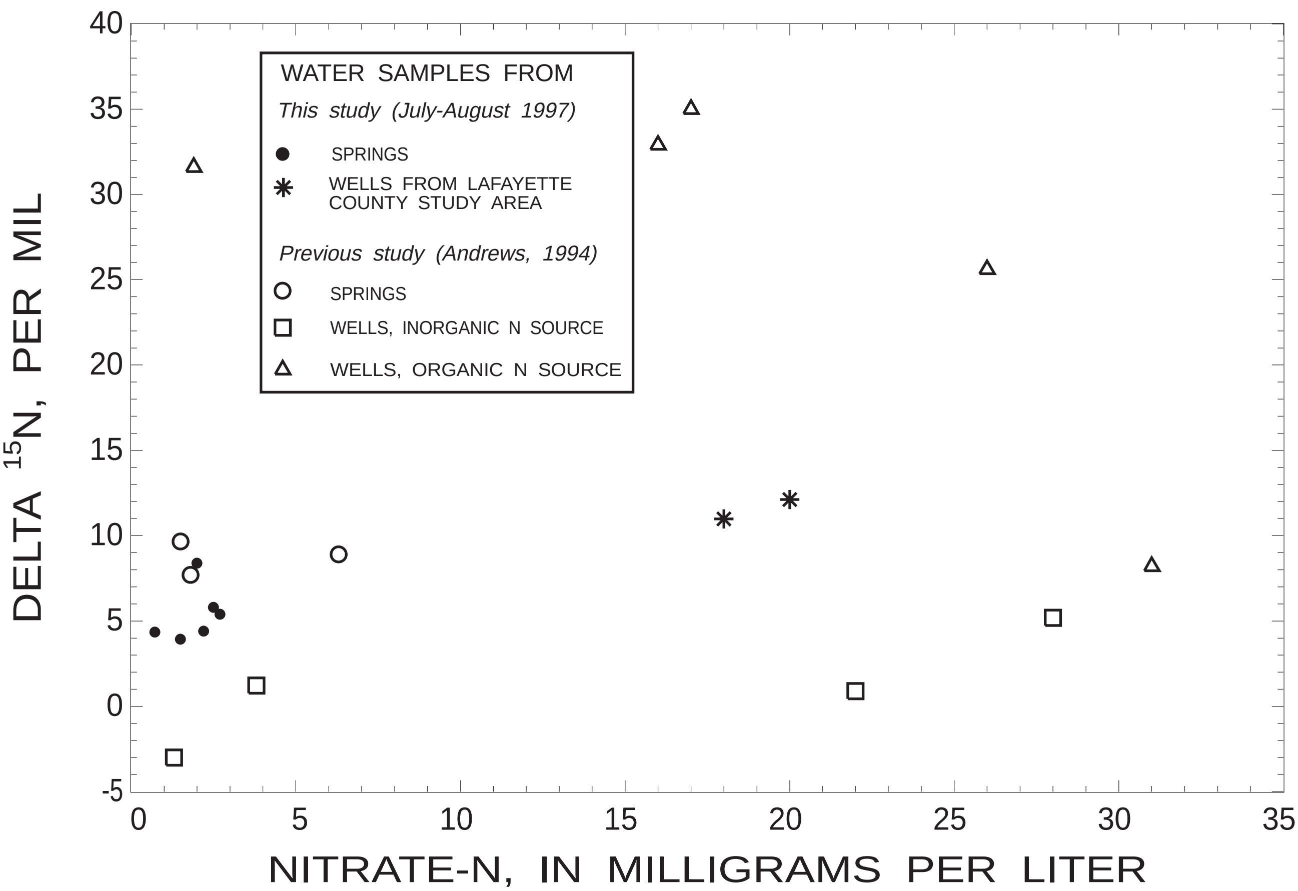

Figure 5. Plot of $\delta^{15}N$ versus NO_3^--N concentrations for springwater and water from zones in the Upper Floridan aquifer.

APPARENT AGES OF SPRINGWATER AND WATER FROM THE UPPER FLORIDAN AQUIFER

Based on CFC-age dating techniques, the mean residence time (age) of water discharging from springs ranges from about 12 to 20 years (fig. 6). The age of water from the two shallow zones in the Upper Floridan aquifer ranges from 12 to 18 years. However, higher than present-day concentrations of CFC-11 and CFC-12 in water from the well -051216011 and of CFC-12 in water from Lafayette Blue Spring (table 4) indicates the likelihood of a local source of contamination of CFCs, possibly from human wastes (Busenberg and Plummer, 1982). Elevated concentrations of N_2O in water from well -051216011 indicate that nitrogen species, such as nitrate from septic tanks, are being transformed to nitrogen gases, possibly due to denitrification reactions in the aquifer.

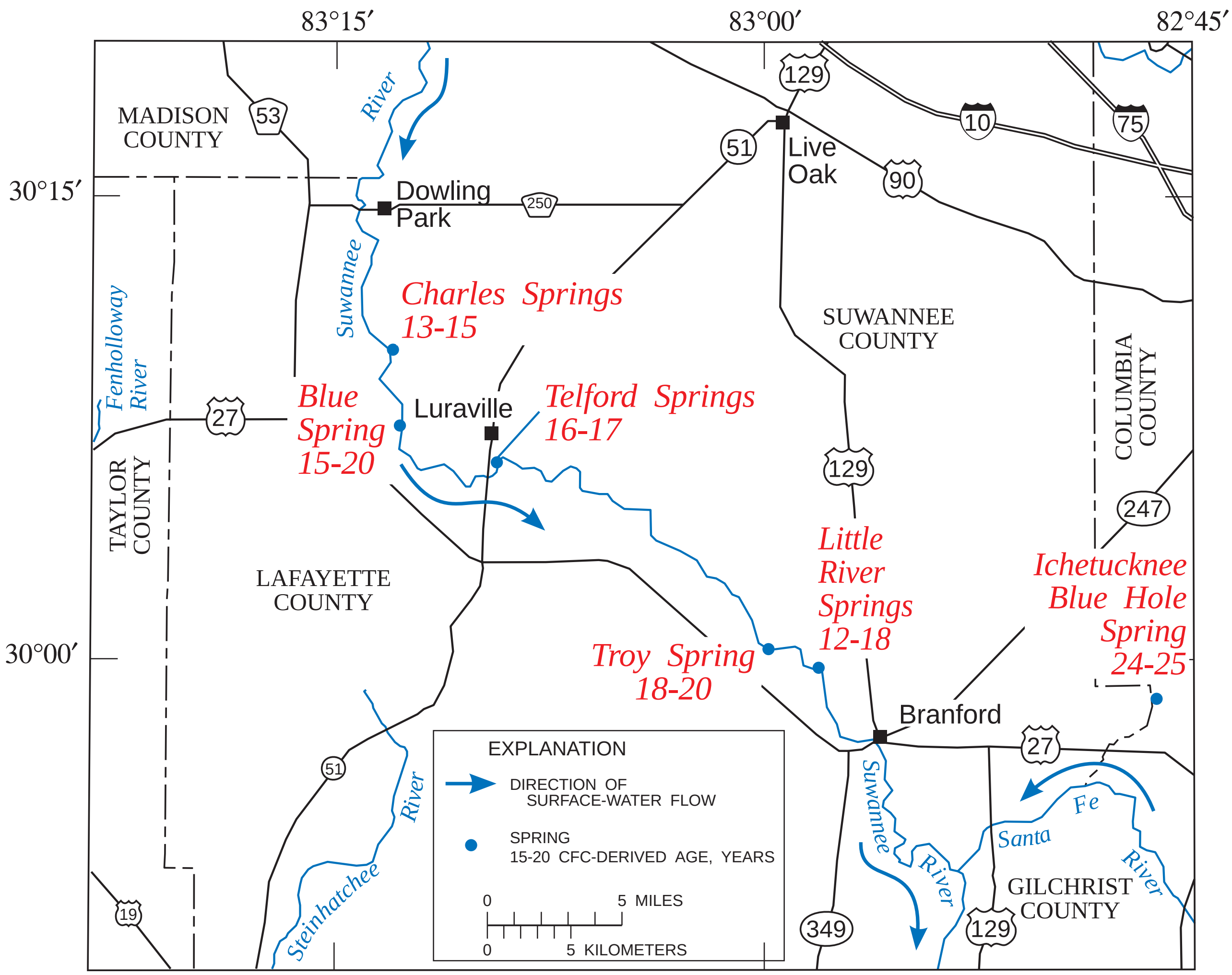

Figure 6. Residence times of water in springs determined from analyses of chlorofluorocarbons.

Table 4. Concentration of CFC-11, CFC-12, and CFC-113 in spring water and water from the Upper Floridan aquifer; calculated atmospheric partial pressure, and model CFC recharge dates.

[Rep. no. denoted replicate number analyzed; pg/kg denotes picograms per kilogram; Alt. denotes altitude of land surface; pptv denotes parts per trillion by volume; Contam. denotes contaminated sample].

Sample name	Rep. no.	Sampling date	Time	Recharge temperature (C)	Alt. (feet)	Concentration in Solution pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Calculated Atmospheric Partial Pressure in pptv CFC-11	CFC-12	CFC-113	Model CFC Recharge Dates CFC-11	CFC-12	CFC-113
Charles Spring	2	07/16/97	1404	20.4	20	201.0	157.5	19.5	115.7	375.4	28.9	1975.0	1984.0	1981.5
Charles Spring	4	07/16/97	1412	20.4	20	199.8	155.2	20.7	115.0	370.0	30.5	1974.5	1983.5	1982.0
Charles Spring	5	07/15/97	1414	20.4	20	201.9	157.9	19.3	116.2	376.4	28.6	1975.0	1984.0	1981.5
Lafayette Blue Spring	2	07/15/97	1616	19.8	20	213.9	315.7	19.0	119.9	735.0	27.2	1975.0	Contam.	1981.0
Lafayette Blue Spring	4	07/15/97	1624	19.8	20	215.7	319.7	17.3	121.0	744.3	24.8	1975.0	Contam.	1980.5
Lafayette Blue Spring	5	07/15/97	1628	19.8	20	222.9	318.0	11.5	125.0	740.5	16.4	1975.5	Contam.	1977.5
Little River Springs	2	07/15/97	904	18.5	20	2518.3	302.4	103.0	1331.1	668.0	138.0	Contam.	Contam.	Contam.
Little River Springs	4	07/15/97	912	18.5	20	152.5	181.9	14.9	80.6	401.9	20.0	1972.0	1985.5	1978.5
Little River Springs	6	07/15/97	920	18.5	20	150.2	178.9	16.9	79.4	395.3	22.7	1972.0	1985.0	1979.5
Telford Spring	2	07/16/97	759	19.5	20	186.9	136.9	17.5	103.4	315.1	24.7	1974.0	1980.5	1980.5
Telford Spring	4	07/16/97	807	19.5	20	185.4	135.7	16.2	102.5	312.1	22.8	1973.5	1980.0	1979.5
Telford Spring	5	07/16/97	811	19.5	20	193.6	140.1	17.7	107.1	322.3	25.0	1974.0	1981.0	1980.5
Troy Spring	1	07/15/97	1005	20.1	20	109.3	141.7	9.7	62.1	333.8	14.2	1970.0	1981.5	1976.0
Troy Spring	3	07/15/97	1013	20.1	20	99.5	121.5	13.5	56.5	286.2	19.6	1969.5	1978.0	1978.5
Troy Spring	5	07/15/97	1021	20.1	20	100.1	126.5	9.9	56.9	298.1	14.5	1969.5	1979.5	1976.5
Ichetucknee Blue Hole	1	08/14/97	1130	20.0	20	119.6	64.7	76.6	67.7	151.8	111.0	1970.5	1971.5	Contam.
Ichetucknee Blue Hole	3	08/14/97	1146	20.0	20	112.2	65.8	28.3	63.4	154.3	41.0	1970.5	1971.5	1984.5
Ichetucknee Blue Hole	6	08/14/97	1216	20.0	20	111.9	65.7	18.5	63.3	154.1	26.7	1970.0	1971.5	1980.5
-051209001	2	07/16/97	1019	20.3	20	277.3	178.8	35.4	158.9	424.6	52.0	1978.5	1986.5	1986.0
-051209001	4	07/16/97	1027	20.3	20	282.4	176.0	34.2	161.8	417.9	50.2	1979.0	1986.5	1986.0
-051209001	5	07/16/97	1031	20.3	20	295.9	184.4	30.2	169.6	437.9	44.4	1979.5	1987.0	1985.0
-051216011	2	07/16/97	1154	25.3	20	695.2	45620.3	36.0	491.1	130517.6	67.5	Contam.	Contam.	1988.5
-051216011	4	07/16/97	1204	25.3	20	690.6	44254.9	37.2	487.8	126611.2	69.8	Contam.	Contam.	1988.5
-051216011	5	07/16/97	1208	25.3	20	670.5	48078.5	37.4	473.7	137550.4	70.1	Contam.	Contam.	1989.0

The concept of an apparent age for water discharging from a spring is considerably more complicated than determining a recharge date for water moving downward by piston flow through an aquifer, assuming a Darcian flow system. A CFC-modeled age for springwaters most likely represents a mean residence time of ground water that results from a mixture of waters with different residence times from various parts of the contributing area for the spring flow system. It is important to note that the ages of springwaters or water from zones in the aquifer represent a value for specific hydrologic conditions. Different ages would most likely be obtained for other hydrologic conditions. Springwater collected during low-flow conditions (extended periods of low rainfall) would probably yield older ages than springwater collected during high-flow conditions (extended periods of high rainfall). The effect of varying hydrologic conditions on ages of springwaters may result from the greater contribution of waters originating from longer ground-water flow paths during low-flow conditions than during high-flow conditions when the contribution of younger waters from shorter ground-water flow paths would probably be greater. Studies of the relative ages of springwaters in the Chesapeake Bay region determined that springwaters are younger during high-flow conditions than during low-flow conditions (Focazio and others, 1997).

Some of the hydrologic and hydraulic factors that affect the relative ages of springwater and water from shallow zones in the Upper Floridan aquifer are (1) the relative contribution of recharge from different parts of the basin; for example, nearby points of focused recharge such as sinkholes (relatively recent recharge) in contrast to water moving along long ground-water flow paths (relatively old recharge), (2) conduit size and distribution, (3) the relation between the heads in the aquifer, the hydraulic gradient, and water levels in the Suwannee River, and (4) the size of the contributing area to a spring. Keeping these factors in mind, the relative ages of springwaters do provide useful information about the size of the contributing area to a spring system. For example, the mean residence time of water from Ichetucknee Blue Hole Spring is longer than that for other springwaters discharging to the Suwannee River. The longer residence time of water in this spring probably indicates that older water from a deeper flow system is mixing with more recently recharged water that results in an average age of 25 years.

Tritium (^3H) concentrations measured in springwater and water from the two zones in the Upper Floridan aquifer were uniform and ranged from about 4.0 to 5.8 TU (table 3). Concentrations of ^3H in ground water in the study area reflect the passing of the ^3H transient through the hydrologic system (fig. 3). Prior to the advent of the atmospheric testing of fusion weapons in 1953, ^3H concentrations were on the order of 2 Tritium Units (TU) or less in this region (Thatcher, 1962). Atmospheric weapons testing during the late 1950’s through the mid 1960’s increased ^3H concentrations in rainfall in this area to a maximum of several hundred TU during the mid-1960's, followed by a sharp decline in concentrations after the nuclear testing moritorium. As pre-bomb water would have a maximum concentration of 0.2 TU at this time, it is evident that all these waters are of relatively recent origin, and almost certainly from the period of the falling limb of the ^3H transient. Accurate dating of the water is not possible due to the lack of a long-term record of the ^3H transient in this area, as well as the slow change in ^3H concentrations over the past decade. Also, measured ^3H concentrations can be affected by hydrodynamic dispersion and mixing of different age waters (Solomon and Sudicky, 1991; Reilly and others, 1994). However, ^3H concentrations found in spring and ground waters are compatible with the estimates of high recharge rates (15 to 31 cm/yr, Grubbs, 1997) and high transmissivity of the Upper Floridan aquifer in the study area (Crane, 1986; Bush and Johnston, 1988).

ADDITIONAL INFORMATION NEEDS AND PLANS FOR FURTHER STUDY

The information obtained from the chemical and isotopic tracers provides the first step in better understanding the sources of nitrate in springs and in shallow zones of the Upper Floridan aquifer. However, this information alone cannot provide a complete understanding of the sources of nitrate and chronology of nitrate loadings to the aquifer system. Knowledge of other factors, such as hydrology and present and historical land

uses, must be integrated with the chemical and isotopic data to obtain a more complete understanding of the factors affecting the concentration of nitrate in springs and in parts of the Upper Floridan aquifer. It is important to emphasize the complexity of the ground-water flow system in this area, and also note that substantial changes in land use have occurred during the past 40 years, which have affected loadings of nitrate to the aquifer during this time. Additional hydrologic information is needed to better understand ground-water paths, rates of ground-water flow, and contributing areas of flow to springs. After contributing areas to springs are estimated, it would be beneficial to obtain information on changes in land use over time so that estimates can be made of temporal and spatial nitrogen loadings to ground water. Several important factors that need to be quantified over time include acreage of cropland, pasture fertilization rates, and number and size of dairy and poultry farms. Loadings of nitrogen to ground water from cropland is related to factors such as crop type, applied fertilizer composition, and rate of fertilizer application. Nitrogen loadings to ground water from dairy and poultry farms are related to factors such as animal populations and waste management practices.

Currently, it remains unclear if the elevated nitrate concentrations in springwaters in the middle Suwannee River area result from past agricultural practices (such as extensive fertilizer application on cropland), recent land uses (for example, disposal of animal wastes from dairy and poultry operations), or a combination of past and present agricultural practices. Additional samples need to be collected for analysis of nitrogen isotopes from springs and shallow and deep zones in the Upper Floridan aquifer. Also, the concentration of nitrate and its isotopic composition in rainfall need to be evaluated to better understand the sources and fate of nitrate in ground water in the Suwannee River Basin.

The next phase of the study will involve sampling of water from approximately 20 sites, including springs, wells, rainfall, and the Suwannee and Santa Fe Rivers. Some springs that were sampled during the first phase of the study will be resampled. The emphasis will be on collecting water samples from additional springs that are discharging water with high concentrations of nitrate to the Suwannee River and Santa Fe River. Also, water samples will be collected from selected wells that are screened in shallow and deep zones of the Upper Floridan aquifer near sampled springs. Contributing areas will be estimated for some of the sampled springs and nitrogen loadings to ground water in the contributing area will be estimated based on historical records of land use and estimates of inputs of nitrogen from fertilizers, human and animal wastes, and atmospheric deposition.

Information on the chemistry of major elements, isotopic composition, redox conditions, and other properties and characteristics of ground water provides a tool for separating certain components in the water that can be attributed to agricultural sources from those resulting from natural processes, such as water-rock interactions. The incorporation of more detailed information, such as the age of water and sources of water and solutes, adds another dimension for interpreting water-quality data. The distribution of nitrate and other solutes can be related to the time ground water was recharged, the origin of the ground water, and its patterns of flow in the aquifer. By combining this information (ground-water ages, sources and flow patterns, and dominant geochemical processes) with hydrologic and land-use information we can obtain a much better understanding of the sources, movement, and fate of nitrate in ground water and surface water in the middle Suwannee River area.

SUMMARY AND CONCLUSIONS

A cooperative study between the Suwannee River Water Management District (SRWMD) and the U.S. Geological Survey (USGS) is evaluating sources of nitrate in water from selected springs and zones in the Upper Floridan aquifer in the Suwannee River Basin. A multi-tracer approach, which consists of the analysis of water samples for naturally occuring chemical and isotopic indicators, is being used to better understand sources and chronology of nitrate contamination in the middle Suwannee River region. In July and August 1997, water samples were collected and analyzed from six springs and two wells for major ions, nutrients, and dissolved organic carbon. Also, these water samples were analyzed for selected environmental isotopes [$^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$] to determine sources of water and nitrate. To better understand when nitrate entered the ground-water system, water samples

are analyzed for chlorofluorocarbons (CFCs; CCl_3F, CCl_2F_2, and $C_2Cl_3F_3$) and tritium (^3H) to assess the apparent ages (residence time) of springwaters and water from the Upper Floridan aquifer.

Delta ^{15}N values for NO_3 in water from the six springs range from 3.94 per mil (Little River Springs) to 8.39 per mil (Lafayette Blue Spring). The range of values indicates that nitrate in the sampled springwaters most likely originates from a mixture of inorganic (fertilizers) and organic (animal wastes) sources; although the higher $\delta^{15}N$ value for Lafayette Blue Spring indicates that an organic source of nitrogen is likely at this site. Water samples from the two wells sampled in Lafayette County have high delta ^{15}N-NO_3 values of 10.98 and 12.1 per mil, indicating the likelihood of an organic source of nitrate. These two wells are located near dairy and poultry farms, where leachate from animal wastes could contribute nitrate to ground water. Based on analysis of CFCs in ground water, the mean residence time of water in springs ranges from about 12 to 20 years. CFC-modeled recharge dates for water samples from the two shallow zones in the Upper Floridan aquifer range from 1985 to 1989.

The multi-tracer approach being used in this study, which integrates chronologic, chemical, and isotopic analyses of ground water, is an important first step in better understanding the sources and fate of nitrate in ground water. The relation between the concentration of nitrate in ground water and the amount of nitrogen that is added to a ground-water basin is affected by hydrogeologic, land-use, climatic and several other factors. Variations in the nitrogen content of water that enters the subsurface over time are related to changes in land use practices, the distribution and effectiveness of natural remediation processes (for example, denitrification), and the distance, direction, and time between recharge to and discharge from ground water. Other critical information that will be collected in the second phase of this study will include delineating the contributing areas for selected springs, assessing the the relative contribution of past agricultural practices and more recent changes in land use, and determining mass-balance loadings of nitrate to ground water.

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